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Molecular dynamics simulations of ordering of polydimethylsiloxane under uniaxial extension

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Abstract

Molecular dynamics simulations of a bulk melts of polydimethylsiloxane (PDMS) are utilized to study chain conformation and ordering under constant uniaxial tension. We find that large extensions induce chain ordering in the direction of applied tension. We also find that voids are created via a cavitation mechanism. This study represents a validation of the current model for PDMS and benchmark for the future study of mechanical properties of PDMS melts enriched with fillers under tension.

Introduction

Polydimethylsiloxane (PDMS) is one of most commonly used silicones for industrial purposes. PDMS has a wide range of applications such as adhesives, coatings, contact lenses, biomedical devices, lubricating oils and heat resistant tiles among many others.¹⁻³ One of the most pronounced features of PDMS is its ability to dramatically change its mechanical properties with the addition of filler to the pure PDMS system. The necessity to understand the deformation and reinforcing mechanisms that control PDMS/filler properties has motivated researchers to investigate, at the molecular level, the changes in structural and dynamical properties influenced by the filler (see e.g. Gee *et al.*⁴). Molecular dynamics (MD) simulations provide an excellent tool to directly study the influence of the filler on material properties upon deformation since contact area between the filler and PDMS is difficult to characterize in experiment.

In this paper, we study bulk PDMS melts upon uniaxial extension via MD simulations. The purpose of this study is to validate the PDMS model and obtain physical insight into the melt behavior upon extension. These results will help rationalize future investigations of silica filled PDMS systems.

Computational Methods

PDMS melt representation and force fields

Polydimethylsiloxane is a macromolecule composed of repeating silicon-oxygen bonds along the backbone.⁵ The chemical structure of the PDMS molecule is $[-O-Si(CH_3)_2-]_n$, where n is the number of repeat units or monomers. The united-atom model representation treats each carbon and its bonded hydrogen atoms as a single united particle. An extensive study of the structural and dynamical properties of a PDMS united-atom model used in this paper is described by Frischknecht *et al.*⁶ This model has shown reasonable agreement with the results of explicit

atom model⁷ for the intermolecular structure, pressure, and chain dimensions in the melt.⁶ Our simulations consisted of 40 120-mer PDMS polymer chains (19,200 total united-atoms), where each monomer contains a single Si, and O united-atom and 2 CH₃ united-atoms.

Molecular dynamics method

Here we use MD to study the structural and dynamic changes in bulk PDMS melts under tension. This is a widely used method for the investigation of various physical processes related to the dynamics of materials (e.g. deformation of solids, polymer crystallization, aging in supercooled liquids, motion of biomolecules). MD provides static and dynamics properties for a collection of particles which allow atomic scale insights that are difficult to gain otherwise.

The amorphous PDMS polymer structures studied here were simulated using 3D cubic periodic boundary conditions. The simulations were generated using constant particle number, pressure, and temperature (*NPT*) dynamics at a pressure of 0 Pa. The velocity Verlet⁸ time integration method was used with a time step of 1 fs. The Andersen⁹ method was used for constant *NPT* dynamics. Specifically, the initial PDMS configuration was generated such that the initial bulk density was taken to be 0.7 g/cm³. The lower density initial state was found to improve the convergence of the equilibration procedure by avoiding high-energy initial configurations. The bulk PDMS ensemble was then initially simulated at 550 K, where the periodic box was allowed to relax under *NPT* conditions. The volume equilibration process was carried out for a minimum duration of 5 ns. Following this step, the system was cooled in *NPT* runs in increments of 50 K and equilibrated for 5 ns each at the incremental temperatures down to 300 K.

After the initial equilibration process, simulations were performed under constant stress, σ , at 300 K in *N σ T* MD runs. The constant stress was applied uniaxially along the y-axis of the periodic simulation cell. The initial periodic simulation cell had dimensions of 8.5 × 8.5 × 8.5 nm. In all extension simulations the applied tensions ranged from 50-80 MPa. The normal stress on the other faces of the simulation box is set to zero. We use a standard Nose-Hoover thermostat and barostat¹⁰. The coupling constants for the barostat and thermostat are 1000 fs and 100 fs respectively, and are kept constant for all extension simulations. All computations were carried out with a modified version of LAMMPS.¹¹

Results and discussions

Uniaxial deformation via a constant stress along the y-axis of the periodic simulation cell is applied to a pure PDMS melt. Figure 1 shows strain (in the direction of applied stress)

$$\lambda(t) = \frac{\Delta L_y(t)}{L_y(0)}$$

as a function of time for the stress range 50-80 MPa at 300 K. The strain λ

develops a shoulder at short times and steadily increases at later times. Similar observations were made in a recent simulation study of a polyethylene (PE) melt under uniaxial extension by Lavine *et al.*¹² The authors investigated crystallization and ordering of PE chains during uniaxial extension and found that “the addition of a large deforming stress accelerates ordering and the crystallization process.” Figure 2 shows “snapshots” of our simulated system at strains of $\lambda = 0$, 1.0, and 1.75 for a relatively low uniaxial stress, $\sigma = 50$ MPa (Figure 2 a)) and a higher stress, σ

= 80 MPa (Figure 2 *b*)). We observe that cavitation occurs at the higher applied stresses consistent with earlier studies of deformation in other polymers.¹³

The dependence of ordering and changes in chain conformation are apparent from visual inspection. Figure 3 shows a single PDMS chain isolated from the melt, at initial configurations (Figure 3 *a*)) and after 0.7 *ns* at $\sigma = 50$ MPa (Figure 3 *b*)) and 0.9 *ns* at $\sigma = 80$ MPa (Figure 3 *c*)). We observe that the chain at $\sigma = 80$ MPa is more elongated compared to the chain at $\sigma = 50$ MPa. In order to quantify the configuration of the chains, we calculated standard chain properties such as end-to-end distance $\langle R_e \rangle$, and the radius of gyration $\langle R_g \rangle$, and find that these quantities increase in time at all stress values displaying a rapid initial rise and a slower increase after that. We also monitored Si-O bond distance as a function of time and uniaxial extension and find that the length is practically constant, as expected, confirming that the bonds are well controlled upon extension.

The chain dynamics are monitored by the evolution of global bond-orientational order parameters $P_2 = \left\langle \frac{3 \cos^2 \theta - 1}{2} \right\rangle$, where θ is the angle between two “chord” vectors and $\langle \dots \rangle$

denotes the average over all chord pairs, and $P_{2y} = \left\langle \frac{3 \cos^2 \theta_y - 1}{2} \right\rangle$, where θ_y is the angle between

the chord vector and the unit vector of the direction in which the tension is applied. A “chord” is defined as a line segment connecting two second nearest neighbors on the same chain (i.e. the vector between the same species in two adjacent monomers). Figure 4 shows time and stress dependence of P_2 and P_{2y} . Both P_2 and P_{2y} increases in magnitude as stress increases, confirming previous observations that the backbones of the polymer chains are rapidly aligned under uniaxial extension.¹² In previous studies of simpler polymers, this results in crystallization. The alignment of the backbone of the chain may be a necessary condition for crystallization, but in the case of PDMS is apparently not sufficient. We do not observe crystallization of PMDS at the time scales we studied. It is possible that mechanisms for crystallization of the PDMS melt are different from the simple polymers and model PE studied in Ref. [12] because of the presence of the two CH_3 groups whose alignment is an important factor for crystallization.

Conclusions

In this paper we present a study of PDMS melt properties upon uniaxial extension. We show that chains become elongated and ordered as a function of applied tension and time. We also find that the PDMS melt cavitates at high tension. The cavity formation is directly related to mechanical properties of the material, therefore addition of filler should effect the cavity formation. Further, we observe changes in the conformation of the backbone as are seen in polyethylene, but we do not observe crystallization, possibly due to the need to reorient the CH_3 groups. We will investigate this in future work.

Acknowledgements

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List of Figure Captions

Figure 1. Strain $\lambda(t) = \frac{\Delta L_y(t)}{L_y(0)}$ measured in the direction of applied tension as a function time for each value of uniaxial tension, σ .

Figure 2. “Snapshots” of our simulations of the PDMS extension. The columns represent system at strain values of $\lambda = 0$ (initial sample), $\lambda = 1$ and $\lambda = 2$, respectively. (a) The applied tension is 50 MPa. , (b) The applied tension is 80 MPa. We observe that the sample cavitates at long times and high value of uniaxial stress.

Figure 3. Single chain conformations at $\sigma = 50$ MPa and $\sigma = 80$ MPa at (a) initial time and strain $\lambda = 0.$, at (b) $\sigma = 50$ MPa, $t = 0.7$ ns and $\lambda=1.75$, and at (c) $\sigma =80$ MPa, $t=0.9$ ns and $\lambda=4.5$. Note that CH_3 groups are not shown for clarity.

Figure 4. Bond-orientational parameters P_2 and P_{2y}

Figures

Figure 1

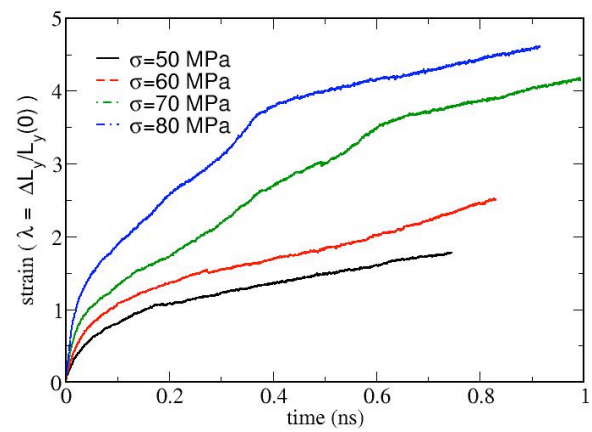


Figure 2

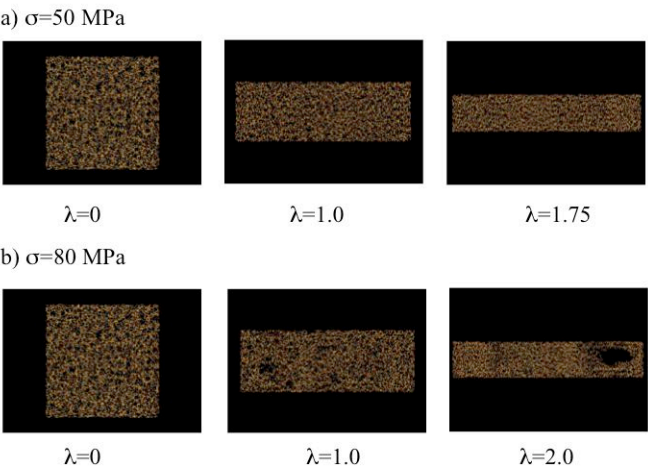


Figure 3

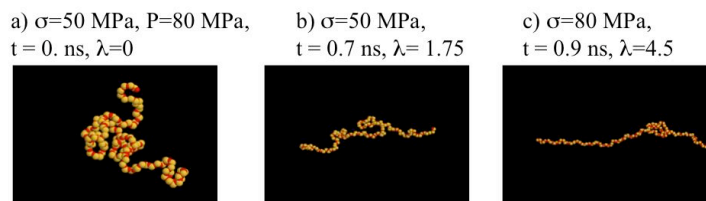


Figure 4

